Comment on "Boson-realization model for the vibrational spectra of tetrahedral molecules"

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Abstract

An algebraic model in terms of a local harmonic boson realization was recently proposed to study molecular vibrational spectra [Zhong-Qi Ma et al., Phys. Rev. A **53**, 2173 (1996)]. Because of the local nature of the bosons the model has to deal with spurious degrees of freedom. An approach to eliminate the latter from both the Hamiltonian and the basis was suggested. We show that this procedure does not remove all spurious components from the Hamiltonian and leads to a restricted set of interactions. We then propose a scheme in which the physical Hamiltonian can be systematically constructed up to any order without the need of imposing conditions on its matrix elements. In addition, we show that this scheme corresponds to the harmonic limit of a symmetry adapted algebraic approach based on $U(2)$ algebras.

PACS numbers: 33.20.Tp, 03.65.Fd

I. INTRODUCTION

In a recent paper [1], Zhong-Qi Ma et al. proposed a model to describe the vibrational spectra of tetrahedral molecules and applied it to the methane molecule. The authors assign to each of the ten interatomic bonds a set of bosonic operators $\{a_i^\dagger, a_i\}$, $i = 1, 2, \ldots, 10$, which satisfy the standard boson commutation relations

$$\left[a_i, a_j^\dagger\right] = \delta_{i,j} , \qquad [a_i, a_j] = \left[a_i^\dagger, a_j^\dagger\right] = 0 . \tag{1}$$

The first four operators $(i = 1, \ldots, 4)$ are chosen to correspond to the C-H bonds (stretching vibrations), while the last six $(i = 5, \ldots, 10)$ represent the H-H bonds (bending vibrations). The Hamiltonian is then expanded in terms of these operators. For methane they proposed the following $\mathcal{T}_d$ invariant Hamiltonian

$$\hat{H} = \hat{H}_1 + \hat{H}_{2s} + \hat{H}_{2b} , \tag{2}$$

where $\hat{H}_1$ is a one-body contribution

$$
\begin{aligned}
\hat{H}_1 = {} & \epsilon_s \sum_{i=1}^{4} a_i^\dagger a_i + \epsilon_b \sum_{i=5}^{10} a_i^\dagger a_i + \lambda_1 \sum_{i \neq j=1}^{4} a_i^\dagger a_j + \lambda_2 \sum_{i \neq j=5}^{10} a_i^\dagger a_j \\
& + \lambda_3 \left[(a_5^\dagger a_8 + a_6^\dagger a_9 + a_7^\dagger a_{10}) + \text{h.c.} \right] \\
& + \lambda_4 \left[a_1^\dagger (a_5 + a_6 + a_7 - a_8 - a_9 - a_{10}) \right. \\
& \qquad + a_2^\dagger (a_5 - a_6 - a_7 - a_8 + a_9 + a_{10}) \\
& \qquad + a_3^\dagger (-a_5 + a_6 - a_7 + a_8 - a_9 + a_{10}) \\
& \qquad \left. + a_4^\dagger (-a_5 - a_6 + a_7 + a_8 + a_9 - a_{10}) + \text{h.c.} \right] \\
& + \lambda_5 \left[(\sum_{i=1}^{4} a_i^\dagger)(\sum_{j=5}^{10} a_j) + \text{h.c.} \right] ,
\end{aligned}
\tag{3}
$$

and $\hat{H}_{2x}$ corresponds to two-body anharmonic contributions to the stretching $(x = s)$ and bending $(x = b)$ vibrations

$$
\begin{aligned}
\hat{H}_{2s} &= -X_s \sum_{i=1}^{4} \hat{N}_i (\hat{N}_i - 1) = -X_s \sum_{i=1}^{4} a_i^\dagger a_i^\dagger a_i a_i , \\
\hat{H}_{2b} &= -X_b \sum_{i=5}^{10} \hat{N}_i (\hat{N}_i - 1) = -X_b \sum_{i=5}^{10} a_i^\dagger a_i^\dagger a_i a_i .
\end{aligned}
\tag{4}
$$

In Eq. (3) we introduced $\epsilon_s = \omega_s - 2X_s$ and $\epsilon_b = \omega_b - 2X_b$. The number operator $\hat{N}_i$ is defined as $\hat{N}_i = a_i^\dagger a_i$. The Hamiltonian conserves the total number of quanta $N = \sum_{i=1}^{10} N_i$. Since the methane molecule has nine vibrational degrees of freedom, while the operators $\{a_i^\dagger, a_i\}$ give rise to ten degrees of freedom, spurious interactions may occur in $\hat{H}$. Their identification, however, is not obvious when the Hamiltonian is written in the form of Eq. (2)–(4). In [1] the authors proceed by identifying the spurious states as those containing the fully symmetric, one-quantum bending state $\psi(A_1; 100000)$ as a factor. With a combination of projection and coupling techniques and an orthogonalization procedure, the physical space up to three quanta is generated. Next it is shown that the physical Hamiltonian does not couple the spurious states with the physical states as long as the conditions

$$\lambda_5 = 0, \qquad X_b = 0, \tag{5}$$

are imposed on the Hamiltonian of Eq. (2). Although these conditions indeed lead to the correct results, they are too restrictive and, furthermore, do not remove all spurious interactions.

II. SPURIOUS INTERACTIONS

In this section, we show that the condition of Eq. (5) is not sufficient to remove all spurious interactions from the Hamiltonian. We define a new set of harmonic bosons with well defined tensorial properties under the tetrahedral $\mathcal{T}_d$ group by projecting the local boson operators. For the stretching modes we have

$$s_{\Gamma,\gamma}^\dagger = \sum_{i=1}^4 \alpha_i^{\Gamma,\gamma} a_i^\dagger, \tag{6}$$

with $\Gamma = A_1, F_2$ and for the bending modes

$$b_{\Gamma,\gamma}^\dagger = \sum_{i=5}^{10} \beta_i^{\Gamma,\gamma} a_i^\dagger, \tag{7}$$

with $\Gamma = A_1, E, F_2$, and similar expressions for the annihilation operators. The coefficients $\alpha_i^{\Gamma,\gamma}$ and $\beta_i^{\Gamma,\gamma}$ are the same as those appearing in the projected wave functions of Eq. (3.1-2)

in [1]. In the framework of this alternative scheme, both the Hamiltonian and the basis states are constructed by repeated coupling of these normal bosons. In this way, we obtain automatically an orthonormal symmetry adapted basis with a well defined number of quanta in each one of the fundamental vibrational modes. For example, with the usual notation for the normal modes of methane $(\nu_1, \nu_2, \nu_3, \nu_4)$, we find for two quanta the following basis states with symmetry A_1

$$|2,0,0,0\rangle = \frac{1}{\sqrt{2}}(s^\dagger_{A_1} s^\dagger_{A_1})^{A_1}|0\rangle \ ,$$

$$|0,2,0,0\rangle = \frac{1}{\sqrt{2}}(b^\dagger_E b^\dagger_E)^{A_1}|0\rangle \ ,$$

$$|0,0,2,0\rangle = \frac{1}{\sqrt{2}}(s^\dagger_{F_2} s^\dagger_{F_2})^{A_1}|0\rangle \ ,$$

$$|0,0,0,2\rangle = \frac{1}{\sqrt{2}}(b^\dagger_{F_2} b^\dagger_{F_2})^{A_1}|0\rangle \ .$$

$$|0,0,1,1\rangle = (s^\dagger_{F_2} b^\dagger_{F_2})^{A_1}|0\rangle \ , \tag{8}$$

Here $(\ldots)^\Gamma$ indicates coupling of two quanta to symmetry Γ. These basis states are orthogonal, since they correspond to eigenfunctions associated with different eigenvalues of the number operators

$$\hat{n}_{\Gamma_s} = \sum_\gamma s^\dagger_{\Gamma,\gamma} s_{\Gamma,\gamma} \ , \qquad \hat{n}_{\Gamma_b} = \sum_\gamma b^\dagger_{\Gamma,\gamma} b_{\Gamma,\gamma} \ . \tag{9}$$

This symmetry adapted procedure provides a method to remove the spurious interactions from the Hamiltonian as well as the spurious states from the basis. It consists in deleting the tensors which are associated with the spurious bending mode, $b^\dagger_{A_1}$ and b_{A_1}, in the construction of physical operators and basis states. This allows an exact elimination of the spurious states without the need to impose additional conditions on matrix elements.

The Hamiltonian of Eq. (2) does include spurious interactions. This can be seen by rewriting $\hat{H}$ in terms of the normal bosons of Eqs. (6) and (7). For the one-body Hamiltonian of Eq. (3) we find

$$\hat{H}_1 = (\epsilon_s + 3\lambda_1)\, \hat{n}_{A_{1s}} + (\epsilon_s - \lambda_1)\, \hat{n}_{F_{2s}}$$

$$+ (\epsilon_b + 5\lambda_2 + \lambda_3)\, \hat{n}_{A_{1b}} + (\epsilon_b - \lambda_2 + \lambda_3)\, \hat{n}_{E_b} + (\epsilon_b - \lambda_2 - \lambda_3)\, \hat{n}_{F_{2b}}$$

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$$+2\sqrt{6}\,\lambda_4\left[(s_{F_2}^\dagger b_{F_2})^{A_1}+\text{h.c.}\right]+2\sqrt{6}\,\lambda_5\left[(s_{A_1}^\dagger b_{A_1})^{A_1}+\text{h.c.}\right]\ . \tag{10}$$

There are two terms that contain the spurious A_1 bending mode. This shows that, in order to remove the spurious interactions from $\hat{H}_1$, the condition $\lambda_5 = 0$ of Eq. (5) is not sufficient. In the present symmetry adapted analysis we find two conditions: $\lambda_5 = 0$ and $\epsilon_b + 5\lambda_2 + \lambda_3 = 0$. We remark that, since the expectation value of $\hat{n}_{A_{1b}}$ in the physical basis vanishes, the omission of the second condition has no further consequences.

A similar analysis can be carried out for the interactions in $\hat{H}_{2s}$ and $\hat{H}_{2b}$. The operators in Eq. (4) represent strong local interactions, and their representation in terms of the normal operators of Eqs. (6) and (7) acquire a complicated form which involves operators that transfer quanta between different modes. The Hamiltonian $\hat{H}_{2s}$ only depends on the stretching modes and hence does not contain spurious interactions. However, the bending contribution $\hat{H}_{2b}$ contains terms that transfer quanta between spurious and physical states. This can be seen by calculating its matrix elements in the basis states with A_1 symmetry that have two quanta in the bending vibrations

$$|\Gamma\rangle = \frac{1}{\sqrt{2}}(b_\Gamma^\dagger b_\Gamma^\dagger)^{A_1}|0\rangle\ , \tag{11}$$

with $\Gamma = A_1$, E and F_2, respectively. The states with $\Gamma = E$, F_2 belong to the physical basis of Eq. (8), whereas the state with $\Gamma = A_1$ is spurious. In this basis the matrix elements of $\hat{H}_{2b}$ are

$$-X_b\begin{pmatrix} \frac{1}{3} & \frac{\sqrt{2}}{3} & \frac{1}{\sqrt{3}} \\ \frac{\sqrt{2}}{3} & \frac{2}{3} & \sqrt{\frac{2}{3}} \\ \frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 1 \end{pmatrix}\ . \tag{12}$$

The nonvanishing matrix elements in the first column and the first row show that $\hat{H}_{2b}$ contains terms which involve the spurious A_1 bending mode. For this reason the parameter X_b in Eq. (4) must vanish in order to remove the spurious contributions from the Hamiltonian, in agreement with the result obtained in [1]. However, this condition also removes the physical part of $\hat{H}_{2b}$ that couples the states with $\Gamma = E$ and F_2.

In summary, in this section we have shown that in order to remove the spurious interactions from the Hamiltonian of [1] three conditions have to be fulfilled

$$\lambda_5 = 0 , \qquad X_b = 0 , \qquad \epsilon_b + 5\lambda_2 + \lambda_3 = 0 . \tag{13}$$

In the calculation of the vibrational spectrum of methane presented in [2], no stretching-bending interactions were included ($X_b = 0$). The spurious components in the Hamiltonian were removed by requiring that its expectation value in the spurious state with one quantum in the A_1 bending mode vanishes. This method only leads to exact results in the harmonic limit in which it reduces to the last condition of Eq. (13).

An additional comment concerns the basis used in [1]. The basis functions in general do not carry the quantum numbers that correspond to the number of quanta in each of the normal vibrational modes. This represents a serious disadvantage in the process of identifying the calculated energies with the experimental ones, which traditionally are reported in terms of these labels. This problem was overcome in [2] by constucting the physical basis by means of the $\mathcal{T}_d$ Clebsch-Gordan coefficients. We note, however, that in Eq. (3.12) of [2] the normalization factor

$$|n\rangle|m\rangle = \prod_\mu \left[\frac{(n_\mu + m_\mu)!}{n_\mu! m_\mu!} \right]^{1/2} |n + m\rangle , \tag{14}$$

was missing. When this factor is included, the coupling procedure provides an orthonormal symmetry-adapted basis for the physical space with the desired labels $(\nu_1, \nu_2, \nu_3, \nu_4)$.

III. SYMMETRY ADAPTED APPROACH

At this point we would like to mention that recently the $U(2)$ model used in [2] has been further developed [3–6] by elaborating a tensorial formalism analogous to the one suggested above. In this symmetry adapted approach the local $U_i(2)$ algebras $\{\hat{G}_i\} \equiv \{\hat{N}_i, \hat{J}_{+,i}, \hat{J}_{-,i}, \hat{J}_{0,i}\}$ are projected to $\mathcal{T}_d$ tensors

$$\hat{T}_{\mu,\gamma}^{\Gamma_s} = \sum_{i=1}^{4} \alpha_i^{\Gamma,\gamma} \hat{J}_{\mu,i} , \qquad \hat{T}_{\mu,\gamma}^{\Gamma_b} = \sum_{i=5}^{10} \beta_i^{\Gamma,\gamma} \hat{J}_{\mu,i} , \tag{15}$$

where $\mu = \pm, 0$. The coefficients have the same meaning as in Eqs. (6) and (7). The $\mathcal{T}_d$ invariant Hamiltonian is constructed by repeated couplings of these tensors to a total symmetry A_1. For example, the interactions that are at most quadratic in the generators and conserve the total number of quanta are given by

$$\hat{\mathcal{H}}_{\Gamma_x} = \frac{1}{2N_x} \sum_\gamma \left(\hat{T}^{\Gamma_x}_{-,\gamma} \hat{T}^{\Gamma_x}_{+,\gamma} + \hat{T}^{\Gamma_x}_{+,\gamma} \hat{T}^{\Gamma_x}_{-,\gamma} \right) ,$$

$$\hat{\mathcal{V}}_{\Gamma_x} = \frac{1}{N_x} \sum_\gamma \hat{T}^{\Gamma_x}_{0,\gamma} \hat{T}^{\Gamma_x}_{0,\gamma} .$$

$$\hat{\mathcal{H}}_{sb} = \frac{1}{2\sqrt{N_s N_b}} \sum_\gamma \left(\hat{T}^{F_{2,s}}_{-,\gamma} \hat{T}^{F_{2,b}}_{+,\gamma} + \hat{T}^{F_{2,s}}_{+,\gamma} \hat{T}^{F_{2,b}}_{-,\gamma} \right) ,$$

$$\hat{\mathcal{V}}_{sb} = \frac{1}{\sqrt{N_s N_b}} \sum_\gamma \hat{T}^{F_{2,s}}_{0,\gamma} \hat{T}^{F_{2,b}}_{0,\gamma} . \tag{16}$$

Here $\Gamma = A_1, F_2$ for stretching vibrations ($x = s$) and $\Gamma = E, F_2$ for bending vibrations ($x = b$). The harmonic limit of these interactions is found by taking the limit $N_i \to \infty$, so that [3,4]

$$\lim_{N_i \to \infty} \frac{\hat{J}_{+,i}}{\sqrt{N_i}} = a_i , \qquad \lim_{N_i \to \infty} \frac{\hat{J}_{-,i}}{\sqrt{N_i}} = a_i^\dagger , \qquad \lim_{N_i \to \infty} \frac{2\hat{J}_{0,i}}{N_i} = 1 , \tag{17}$$

where a_i and $a_i^\dagger$ are the boson operators used in [1]. In this harmonic limit the interactions of Eq. (16) take the form

$$\lim_{N_s \to \infty} \hat{\mathcal{H}}_{\Gamma_s} = \frac{1}{2} \sum_\gamma \left(s^\dagger_{\Gamma,\gamma} s_{\Gamma,\gamma} + s_{\Gamma,\gamma} s^\dagger_{\Gamma,\gamma} \right) ,$$

$$\lim_{N_b \to \infty} \hat{\mathcal{H}}_{\Gamma_b} = \frac{1}{2} \sum_\gamma \left(b^\dagger_{\Gamma,\gamma} b_{\Gamma,\gamma} + b_{\Gamma,\gamma} b^\dagger_{\Gamma,\gamma} \right) ,$$

$$\lim_{N_x \to \infty} \hat{\mathcal{V}}_{\Gamma_x} = 0 ,$$

$$\lim_{N_s, N_b \to \infty} \hat{\mathcal{H}}_{sb} = \frac{1}{2} \sum_\gamma \left(s^\dagger_{F_2,\gamma} b_{F_2,\gamma} + s_{F_2,\gamma} b^\dagger_{F_2,\gamma} \right) ,$$

$$\lim_{N_s, N_b \to \infty} \hat{\mathcal{V}}_{sb} = 0 . \tag{18}$$

which corresponds to the interactions appearing in Eq. (10), with the exception of the spurious interaction which, by construction, does not arise in this approach [6]. The symmetry adapted basis states are constructed as in [2], but now taking into account the appropriate

normalization coefficients of Eq. (14). The application of this model to the vibrational spectrum of methane yields a fit which is an order of magnitude more accurate than those of [1] and [2].

IV. SUMMARY AND CONCLUSIONS

Summarizing, we have analyzed the boson realization model presented by Zhong-Qi Ma et al. in [1] and found the following results:

(i) The approach presented in [1] does not remove all spurious interactions from the Hamiltonian. Moreover, the condition $X_b = 0$ eliminates, in addition to spurious interactions, also some physical interaction terms.

(ii) Although the method proposed to remove the spurious states gives the correct results, it becomes increasingly difficult to apply when additional higher order interactions have to be included in the Hamiltonian.

(iii) In general, the basis in which the Hamiltonian is diagonalized does not carry the quantum numbers associated to the number of quanta in each fundamental vibrational mode. This problem can be solved either by using the $\mathcal{T}_d$ Clebsch-Gordan coefficients or by diagonalizing the number operators of Eq. (9).

(iv) The formulation in terms of tensor operators provides a natural way to eliminate the spurious interactions from the Hamiltonian. Besides, we have shown that the approach of [1] corresponds to the harmonic limit of a more general method based on coupled $U(2)$ algebras [3–6].

ACKNOWLEDGEMENTS

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